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## Free-volume hole model for positronium formation in polymers: surface studies

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**Abstract.** Positron annihilation lifetime and Doppler broadening of annihilation radiation experiments are performed in a polyurethane film using the mono-energetic slow positron probe as a function of positron energies. Significant variations of positron annihilation signals are observed at a short distance from the surface (<100 nm). The ortho-positronium lifetime in the polymer increases near the surface, while its intensity decreases. The intensity results are consistent with the description of a free-volume hole model for positronium formation proposed by Brandt, Berko and Walker. This study further confirms that positron annihilation spectroscopy is a sensitive probe for the characterization of physical properties of sub-nanometre defects, such as free volumes and holes for polymeric materials.

### 1. Introduction

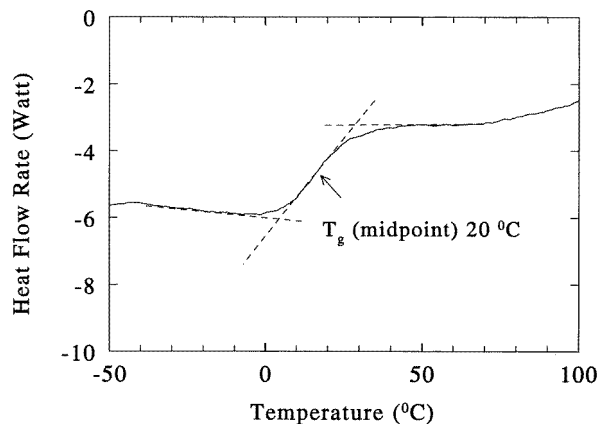
In recent years, positron annihilation spectroscopy (PAS) has been developed as a useful tool in probing the nanoscopic and local properties of polymeric materials. One of the great successes in this line of research is the determination of defect properties, such as free volumes and holes, at an atomic scale (0.2–2 nm) in polymers. It has been demonstrated that positron annihilation lifetime (PAL) spectroscopy is capable of determining size, distribution and fraction of holes and free volumes in polymers [1–8] while the angular correlation of annihilation radiation provides the anisotropy information of these sub-nanometre structures [9, 10]. The high sensitivity of PAS in probing defect properties arises from the fact that the positronium atom (Ps, an atom consisting of a positron and an electron) is preferentially trapped (localized) in atomic-scale free volumes and holes.

Applications of PAS to determine the physical properties of the surface and the bulk require basic understanding of the formation mechanism of Ps in polymeric materials. A free-volume model was proposed in 1960 by Brandt *et al* [11, 12] who proposed that Ps is formed only in an open space of molecular substrates, the so-called ‘free volume’. This model has been later adopted to describe both the free-volume (i.e. dynamic hole in polymers) and hole (i.e. a general term for any open space) properties in polymeric materials as deduced from PAS method. To be comparable with the existing terms in polymer science, here we use a general term of ‘free-volume hole model’ to include both free volumes and holes commonly used. Recently, some questions about the validity of this model to describe

the free volume in polymers have been raised by Yee *et al* [6]. The purpose of this paper is to re-examine the validity of the free-volume hole model for the description of Ps formation based on newly obtained data by using the slow positron coupled with lifetime spectroscopy. We also include discussions comparing with other proposed models for Ps formation, which may not be apt to derive the free-volume and hole information from PAS data.

## 2. Experiments

The polyurethane samples were prepared by using N-3300 di-isocyanate and 670 A-80 polyester polyol in the equivalent ratio 1.05:1 (purchased from Bayer Chemical, Allentown, PA) with the following specifications: density =  $1.100 \times 10^3 \text{ kg m}^{-3}$ ,  $M_w = 4200$ . The  $T_g$  of the bulk was determined using a DSC (Polymer Labs, model 3) at a scanning rate of  $10^\circ\text{C min}^{-1}$ . The resulting  $T_g$  value is  $20.0 \pm 1.0^\circ\text{C}$  from the mid-point of the discontinuous change in the DSC measurement as shown in figure 1. The positron annihilation lifetime (PAL) in the same bulk polyurethane was measured at room temperature ( $23^\circ\text{C}$ ) using the conventional PAL method as described elsewhere [13]. The lifetime results are:  $\tau_1 = 0.125 \text{ ns}$  (fixed);  $\tau_2 = 0.410 \pm 0.08 \text{ ns}$ ;  $I_2 = 50.0 \pm 0.4\%$ ;  $\tau_3 = 2.30 \pm 0.05 \text{ ns}$ ;  $I_3 = 24.0 \pm 0.2\%$ . This is in agreement with the existing PAL data in some polyurethanes [14].



**Figure 1.** A DSC plot of heat flow rate against temperature for polyurethane.

The thin film samples were prepared under a dry  $\text{N}_2$  environment by solvent spinning polyurethane dissolved in acetone onto a copper sheet at a speed of 1000 rpm. The prepared film sample (thickness  $\sim 30 \mu\text{m}$ ) coating the Cu sheet was cured at r.t. inside a vacuum furnace for 24 h before it was mounted in the beam line for the positron measurements.

The positron annihilation lifetime (PAL) data were recorded at the intense slow positron facility in the Electrotechnical Laboratory (ETL) [15], and the Doppler broadening energy spectra (DBES) data at were recorded at Brookhaven National Laboratory [15]. The lifetime resolution is 250 ps at a counting rate of 1000–1500 cps ( $1 \mu\text{A}$  of electron linac current). Each PAL spectrum was collected for a period of  $\approx 10$  minutes for a total of approximately  $10^6$  counts. Detailed descriptions of PAL coupled with a slow positron beam are given elsewhere [15]. The obtained PAL spectra were fitted into three to four lifetimes using PATFIT programs [16]. Two series of PAL spectra were acquired, short-gated (26 ns)

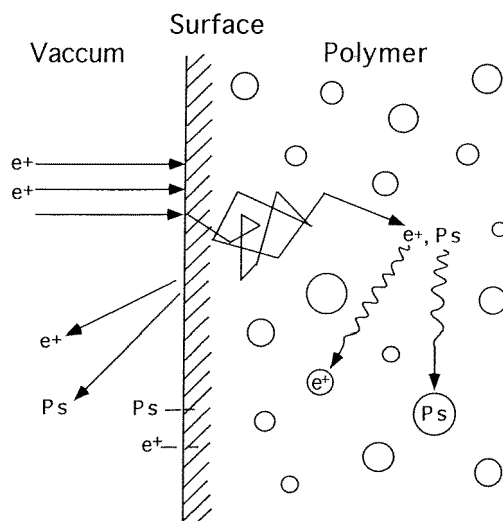
and long-gated spectra (800 ns), to search for near surface Ps and free Ps in a vacuum, respectively. The PAL results which fit best are expressed in four lifetimes.

For DBES and PAL experiments, the vacuum of the sample chamber was about  $10^{-6}$  and  $10^{-8}$  Torr at high and low temperatures, respectively. The DBES spectra were recorded at r.t. (23 °C) as a function of positron incident energies. The DBES spectra were recorded using a HP Ge detector (from EG&G Ortec, with a 35% efficiency and an energy resolution of 1.5 keV at 511 keV peak) at a counting rate of about 1500 cps. The total count of each DBES was 0.5 million. The obtained DBES spectra are expressed in an  $S$  parameter, which is defined as a ratio of integrated counts between 509.41 and 512.59 keV (the central part) to the total counts in the photon peak after the background was properly subtracted. Since the  $S$  parameter represents the relative value of the low-momentum part of positron–electron annihilation radiation, it is sensitive to the change of positron and Ps states due to microstructural changes. When the positron and Ps are localized in a hole or free volume with a finite size, the observed  $S$  parameter is a measure of the momentum broadening according to the uncertainty principle: a larger hole results in a smaller momentum distribution and thus a larger value of  $S$  parameter. The  $S$  parameter is obtained from the central part of the  $2\gamma$  peak. Detailed experimental results of DBES coupled with a slow beam are described elsewhere [17, 18].

### 3. Results and discussion

#### 3.1. Implantation of the positron

When a mono-energetic positron is implanted from a vacuum to a polymer film, the positron survives before annihilation either as a unbounded positron, or in the form of a positronium atom (Ps) by picking up an electron from molecules. Four possible locations for the positron and Ps before the annihilation are: (1) the polymer bulk matrix, (2) a defect, such as a hole or free volume, (3) on the surface or (4) the vacuum. This is schematically shown in figure 2.



**Figure 2.** A schematic diagram for the positron and Ps states near the surface of polymers.

As shown in figure 2, detection of the positron and Ps states is more complicated in polymers than it is in semiconductors or metals, where there is no Ps formation in the bulk. Therefore, it becomes necessary to use more than one detection technique in order to extract microstructural information from positron results. The inelastic collision between the positron and molecules slows down the energy via ionization, excitation and phonon processes. The implantation stopping profile  $P$  varies as a function of depth as [17]:

$$P(z, E) = -d [\exp -(z/z_0)^2]/dz \quad (1)$$

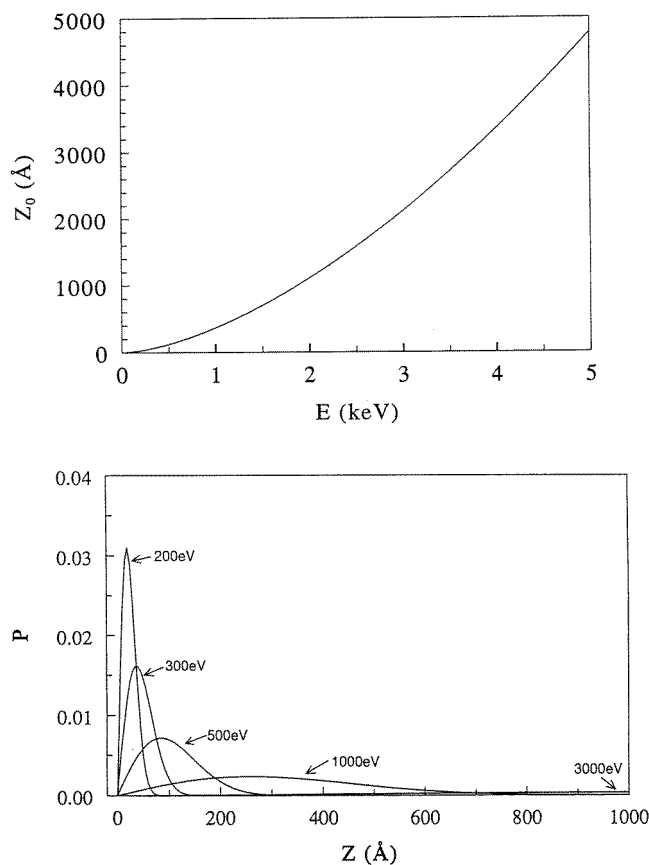
where  $z_0$  is related to the mean implantation depth  $Z_0$  through:

$$z_0 = 2Z_0/\sqrt{\pi}. \quad (2)$$

$Z_0$  depends on incident energy as [17]:

$$Z_0(E) = (400/\rho)E^{1.6} \quad (3)$$

where  $Z_0$  expressed in  $\text{\AA}$ ,  $\rho$  is the density in  $\text{g cm}^{-3}$ , and  $E$  is in keV. Figure 3 shows the relationships between  $Z_0$  and  $E$ , and between  $P(z, E)$  and  $z$  for polyurethane. For example, at the very low energy  $E$  of 0.2 keV, the positron penetrates only 27  $\text{\AA}$  from the surface. The dispersion of the depth profile increases quickly as the positron energy increases. In

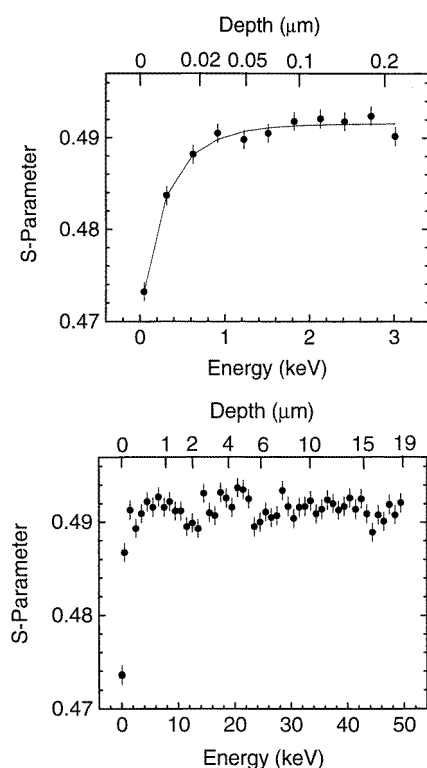


**Figure 3.** Mean stopping distance  $Z_0$  as a function of incident positron energy (top) and the stopping profile  $P(z)$  at different incident positron energy in polyurethane (lower).

other words, the resolution defining the depth decreases quickly as the distance increases from the surface.

### 3.2. DBES results

The variation of  $S$  parameter with the implanted energy is shown in figure 4. As the positron energy increases, the fractions of both positron and p-Ps (singlet Ps) annihilating in the polymer increase. Therefore we observe an increase of  $S$  parameter with energy at very low energy levels (near the surface) and reaching a plateau at medium energy levels (the bulk). A large variation of  $S$  parameter at low energy (<2 keV) indicates a significant variation of free-volume hole structures and positron behaviour near the surface ( $\leq 100$  nm). By fitting the  $S$  parameter to a simple diffusion model using the computer program VEPFIT [19], we obtained a mean positron and Ps diffusion length  $= 15.8 \pm 1.1$  nm. This is rather short compared with those in semiconductors and metals which are of the order of hundreds of nanometres [17].

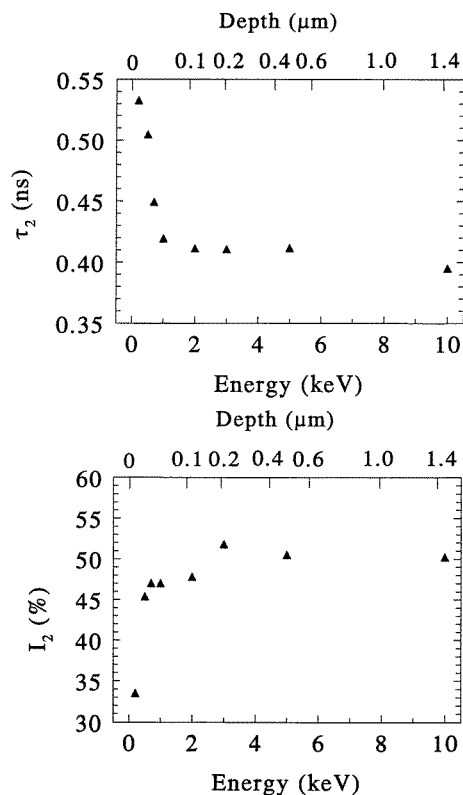


**Figure 4.**  $S$  parameter from DBES against positron incident energy of polyurethane thin film ( $\sim 30 \mu\text{m}$ ) on Cu substrate. The line was fitted to a simple diffusion model from the VEPFIT program [19].

### 3.3. PAL results

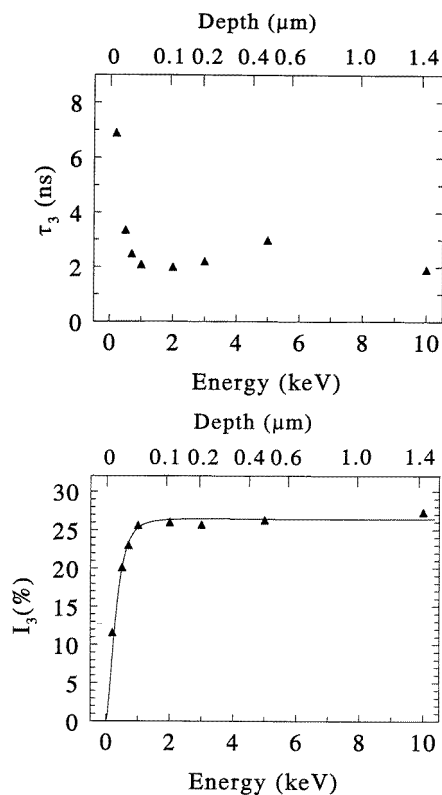
The PAL spectra were first fitted into four lifetimes without any constraint. In the long-gated PAL spectra, we obtained the longest lifetimes of ( $\tau_4$ )  $\approx 60$ – $150$  ns, and they do not change

systematically with the energy as intensity ( $I_4$ ) does. In order to obtain information about polymeric properties, we then analysed all PAL data into four components by constraining  $\tau_1 = 0.125$  ns and  $\tau_4 = 142$  ns (the free o-Ps lifetime).  $\tau_1$  and  $\tau_4$  are attributed to p-Ps annihilation and o-Ps emitted from the surface, respectively. Two intermediate lifetimes,  $\tau_2 \approx 0.35$ – $0.55$  ns and  $\tau_3 = 2.0$ – $10.0$  ns, are attributed to the positron and the o-Ps annihilation in the polymers, respectively.



**Figure 5.**  $\tau_2$  and  $I_2$  against positron energy in a polyurethane film at r.t. Errors are smaller than the sizes of data points shown.

Figures 5–7 show the variations of  $\tau_2$ ,  $I_2$ ,  $\tau_3$ ,  $I_3$  and  $I_4$  with respect to the positron incident energy in polyurethane at r.t. As shown in figure 5,  $\tau_2$  increases near the surface while  $I_2$  decreases. Similarly,  $I_3$  decreases and  $\tau_3$  increases significantly as the energy decreases (figure 6). On the other hand,  $I_4$  increases as the energy decreases (top of figure 7), opposite to the case of  $I_3$ . It is interesting to observe that the sum of  $I_3$  and  $I_4$  is roughly constant as a function of energy except at a very low energy (0.2 keV), as shown in figure 7 (bottom). This indicates that most of the Ps formed inside the polymer is not able to escape to the vacuum (to be discussed later). Although in clean metal or semiconductor surfaces, Ps is mainly formed from the surface, the situation in polymers could be very different when one considers their large fraction of defects (2–20%). The holes and free volumes become effective sites to trap positrons for Ps formation. In this case, the Ps formed on the surface of polymers becomes a small fraction except at a distance very near the surface ( $\approx 3$  nm).



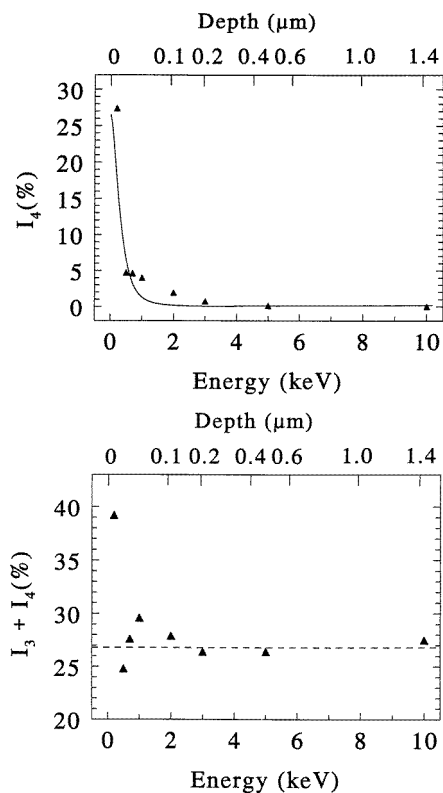
**Figure 6.**  $\tau_3$  and  $I_3$  against positron energy in a polyurethane film at r.t. The line through  $I_3$  was fitted by using an equation  $=QI_3(\text{bulk})$ ,  $I_3(\text{bulk}) = 26.5\%$ , and  $Q$  is equation (5) according to a simple positron stopping/diffusion model. Errors are smaller than the sizes of data points shown.

Before we discuss the second and third components of PAL data, it is important to confirm that  $I_4$  is due to  $3\gamma$  annihilation from o-Ps re-emitted to the vacuum. This is established by looking for consistency with the DBES spectra. The fraction of o-Ps in the vacuum could be obtained from the  $R$  parameter, which is defined as the fraction of  $3\gamma$  to the total annihilation of DBES. The o-Ps fraction in a vacuum,  $f$ , could be calculated from  $R$  parameters by using the following equation [17]:

$$f = [1 + (p_1/p_0)(R_1 - R)/(R - R_0)]^{-1} \quad (4)$$

where  $R_1$  and  $R_0$  are the  $R$  parameters for 100% and 0% Ps formation in a vacuum, respectively, and the  $2\gamma$  peak ratio is  $p_1/p_0 = 0.21$  for the currently used slow beam for 100% and 0% Ps formation. The  $R_1$  was determined to be 7.0 from high purity Al samples at high temperature–low energy, and  $R_0$  was determined to be 2.40 from the DBES at high energy. The  $R$  parameter and calculated  $f$  are plotted in figure 8. As shown there, the variation of  $f$  from DBES with respect to the energy is very similar to  $I_4$  from PAL data (top of figure 7).



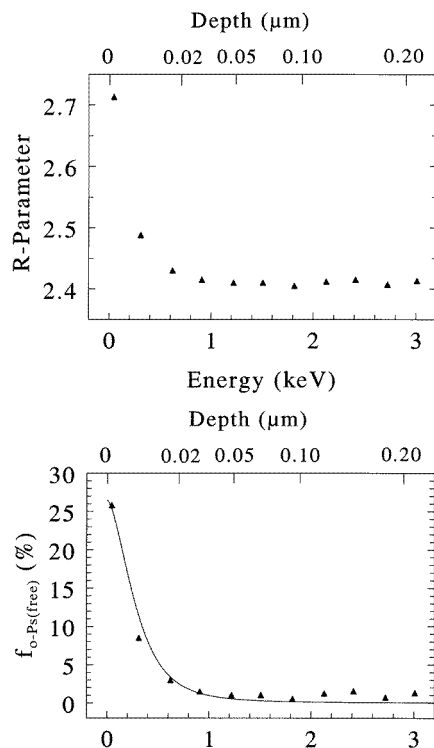


**Figure 7.**  $I_4$ (free o-Ps fraction) and  $I_3 + I_4$  (total o-Ps intensity) against positron energy of polyurethane at r.t. The solid line (top) was fitted by using an equation  $= (1 - Q)I_3(\text{bulk})$ ,  $Q$  is equation (5) and  $I_3(\text{bulk}) = 26.5\%$ . The dashed line (bottom) was drawn through data except the point at 0.2 keV, Errors are smaller than data points shown.

### 3.4. Ps formation in polymers

The increase of  $I_3$  (bottom of figure 6) with respect to the energy is expected from the point of view of that o-Ps formation increases as the percentage of positrons stopped in the polymer increases. The increasing fraction of o-Ps in the polymer is consistent with the increasing  $S$  parameter (top of figure 4), which detects the fraction of the other form of Ps, p-Ps. The intensity of p-Ps in the polymer is one-third that of o-Ps. The variation of  $I_3$  with respect to energy provides information about the formation mechanism in polymers.

There are three existing models to describe Ps formation in polymers: the free-volume hole, the hot and the spur models. According to the original Ps free-volume model by Brandt, Berko and Walker [11], Ps is formed in an open space, such as a vacancy, hole or free volume. It is formed by abstracting an electron from the surface of holes or free volumes. This is schematically shown in the upper part of figure 9. Its mechanism is similar to the Ps formation from the surface by an abstraction reaction before the positron leaves the vacuum. In polymers, holes and free volumes have inner surfaces which are analogous to the surface and the vacuum. It is known that epithermal Ps can be formed from non-thermalized positrons diffusing back to the surface [20, 21]. Similarly, the energy of the positron which forms Ps in holes and free volumes could be at the hot or epithermal stage.



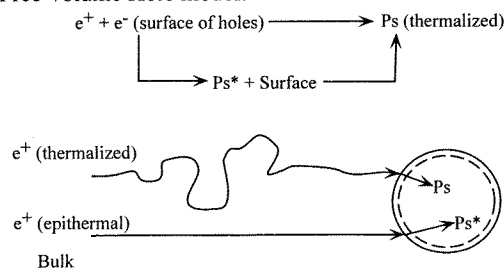
**Figure 8.**  $R$  parameter from DBES against positron energy (top) and the calculated free o-Ps fraction in the vacuum (bottom) from polyurethane. The line was fitted by using an equation  $= (1 - Q)I_3(\text{bulk})$ ,  $Q$  is equation (5) and  $I_3(\text{bulk}) = 26.5\%$ . Errors are smaller than the sizes of data points.

The probability of the positron abstracting electrons from the inner surface may be also energy dependent. It is conceivable that Ps formation is more favourable for positrons with a lower energy than a higher one as observed in clean metallic and semiconductor surfaces [17]. In this model, the free volume or hole also serves as a reservoir to accommodate the energy requirements for the whole process of Ps formation and slowing down. The formed epithermal Ps will continue to lose its energy by colliding with the inner surfaces of the holes until it is thermalized, and eventually it annihilates in sub-nanometre holes, free volumes of polymers through  $2\gamma$  or in vacuum or a large void through  $3\gamma$ . According to this model, the o-Ps intensity can be a measure of the fraction of free volumes and holes (or any defect) if the probability of escape from the trapped hole to another hole is small. This has recently been shown to be the case according to Ps diffusion data [22] and quantum calculations [7, 23].

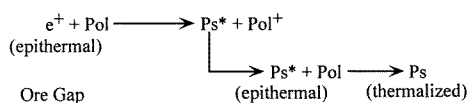
The second (hot) model was proposed by Ore and Powell in 1949 [24], who used a simple thermodynamic concept that Ps formation is possible only when the positron falls within an energy gap between the ionization energy ( $I$ ) and the energy of  $I$  minus the binding energy of Ps. The upper energy limit occurs because the process of ionization dominates Ps formation. The lower limit is due to gain in the Ps formation, e.g. the binding energy  $= 6.8$  eV in the case of free Ps. In polymers, the energy gap is modified by the dielectric constant (which narrows the energy gap for Ps formation) and the zero point energy due to Ps localization in holes (which reduces the Ps binding energy) [25]. This model is

## Ps formation mechanisms in polymers

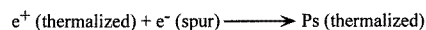
### I. Free-volume Hole model:



### II. Abstraction (Hot) model:



### III. Direct combination (Spur) model:



Spur

**Figure 9.** A schematic diagram for three Ps formation models discussed in this work for polymers.

called the hot model because of its large energy (1–20 eV) relative to the thermal energy. The mechanism of this model can be also expressed as an abstraction reaction between the epithermal positron and molecules (bulk). This is similar to hydrogen formation by a sequential charge exchange process between the energetic proton and molecules. This model is schematically shown in the middle part of figure 9. It is worthwhile to mention differences between the free-volume hole and the Ore model: (1) the Ore model has an energy gap allowing for Ps formation, while the free-volume hole model does not have a threshold energy; (2) the Ps is formed in the bulk prior to the localization to the hole according to the Ore model, while the free-volume hole model allows Ps to form in a hole only and (3) in the Ore model, Ps formation depends on the physical properties, such as dielectric constant and energy levels of polymers, while the free-volume hole model depends on the local molecular and hole structures of polymers.

In the third (spur) model, Ps forms through a direct combination between the positron and the secondary electrons in the positron track when it is slowing down [26]. The encounter probability between the positron and the electrons in the radiation track depends on a size, defined as the Onsager distance [25]. At this distance, it is such that the positron and electrons are still more likely to attract each other than they are to randomly escape. This model has received great attention for Ps formation in liquids because it relates to the chemical properties and radiation effects of molecules [25]. In radiation chemistry of liquids, this is often called the spur model. According to the spur model, it is expected that the majority of Ps formation occurs from thermalized positrons where a large spur has

formed. A key difference between the first two models and the spur model is the positron energy at the point of Ps formation. The positron is mainly at the thermal stage for the spur mechanism while it is at the epithermal stage for the hot model, and it can be at both epithermal and thermal stages for the free-volume hole model. Consequently, the o-Ps intensity is directly related to the spur size at the end of the positron track. The spur model is also schematically shown in the lower part of figure 9 for comparison with the others.

The  $I_3$  data against the positron incident energy provide us with clues to address the suitability of these models. In general, a decrease of  $I_3$  near the surface is expected because a smaller number of incident positrons penetrate the bulk of polymers. However, the properties which affect  $I_3$  variation with respect to  $E$  will be quite different among these three models. In the free-volume hole model, the variation simply depends on the stopping probability; in the hot model the variation is modified by the energy levels of the polymer; in the spur model, it depends on both electronic and chemical properties of polymers.

The probability of the positron being stopped in a polymer  $Q(E)$  is an integral of the stopping profile. Since the positron stopping profile  $P(z, E)$  as shown in equation (1) is a Gaussian function, the fraction of the positron stopped in the polymer could be obtained by integrating  $P$  and a function describing the flux of the positron diffusing back to the surface. With this consideration, an analytical equation for the fraction of the positron stopped in the substrate has been derived [17, 27]:

$$Q(\sigma_g) = \pi^{1/2} \sigma_g \exp(\sigma_g^2) \operatorname{erfc}(\sigma_g) \quad (5)$$

where  $\operatorname{erfc}$  is the complimentary error function, and

$$\sigma_g = \frac{Z_0}{L_+ \pi^{1/2}}. \quad (6)$$

As above,  $L_+$  is the positron diffusion length in the polymer. From this theoretical analysis, the intensity of Ps formation in polymers ( $I_3$ ) is expected to increase very rapidly as a function of  $E$ . Without invoking any model for the Ps formation mechanism, we first fit the  $I_3$  variation with respect to energy using an equation  $= Q I_3(\text{bulk})$ , where  $I_3(\text{bulk})$  is the  $I_3$  at high energy, which is 26.5% from data shown in figure 6 (bottom). We obtain a fitted value  $L_+ = 6.8 \pm 1.0$  nm and plot the curve in figure 6 (bottom). From this diffusion length, we then calculate the diffusion coefficient according to the one-dimensional motion equation:

$$L_+ = \sqrt{D_+ \tau_+}. \quad (7)$$

The calculated  $D_+ = 1 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$  for the positron in polyurethane. These diffusion coefficients are consistent with the experimental positron mobility data ( $\sim 0.1\text{--}0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) in amorphous polymers from the electric field dependence of DBES [28].

Since the sum of  $I_3$  and  $I_4$  is roughly constant except very near the surface (bottom of figure 7), we examine the  $I_4$  from PAL and  $f_{o-Ps}$  from DBES in terms of the positrons escaping to the surface using the same positron diffusion model as described above. In this model,  $I_4$  and  $f_{o-Ps}$  can be expressed as  $(1 - Q)I_3(\text{bulk})$ , where  $I_3$  is taken as the o-Ps intensity (26.5%) at high energy. As shown in figures 7 (top) and 8 (bottom), we find the data fit well with the same diffusion length ( $L_+ = 6.8$  nm) as  $I_3$  data do. The consistent description of  $I_3$ ,  $I_4$  and  $f_{o-Ps}$  data in terms of a simple positron stopping and diffusion model sheds light on the Ps formation mechanism in polymers.

Let us first consider the possibility of the spur model for Ps formation in polymers. In this model, Ps formation depends on both the diffusion of the positron and the mobility of electrons in the spur. If secondary electrons in the spur are involved in Ps formation, then

the  $L_+$  obtained by fitting  $I_3$  against  $E$  should be a sum of the actual positron diffusion length and the spur size. Typical spur size is of the order of a few hundred Å for electrons and positrons [29]. Xie *et al* [29] arbitrarily invoked a simple exponential function to fit for  $I_3$  against  $E$  variation and obtained a very large value of length (66 nm) which was linked with a combined distance between positron and electrons in polymers. These authors further defined this fitted length as the spur size and described Ps formation as occurring through a spur process. The current data and interpretation give a very different result. The fitted length (6.8 nm) is one order of magnitude smaller than theirs and is consistent with the positron diffusion length estimated from the positron mobility data in polymers. Not only do we have three times better lifetime resolution in the present PAL experiments than theirs, but also we analyse the data with a sound theoretical model. This analysis raises a serious question as to what extent that the formation of Ps in polymers is involved with the spur mechanism. The possible involvement of the spur process is through those excess electrons trapped in free volumes and holes for thermalized positrons to form Ps as part of the free-volume hole model.

Because of the obtained short distance for the positron and electron distance in forming Ps from the current  $I_3$ ,  $I_4$  and  $f_{o-Ps}$  data analysis, the positrons, which form Ps with electrons, have essentially no mobility. From this notion, these electrons are unlikely to be the secondary electrons in the terminal spur as discussed above, otherwise they should have a much larger value of length (of the order of 50–100 nm, the spur size) than the currently obtained  $L_+$  (6.8 nm). The best candidates for the electrons which form Ps are those still bounded in the surface of holes and free volumes. These electrons have low mobility and do not contribute to the obtained  $L_+$ , which can be solely described by the positron mobility alone. This analysis leads us to conclude that the spur process does not play a significant part in the Ps formation in polymers.

Next we discuss the possibility of Ps formation in terms of the free-volume hole and hot models. The current PAL experimental data do not provide sufficient information to differentiate them because both models say that Ps could be formed at the epithermal stage and through an abstraction process. The key difference is that the electron is from the inner surface of holes in the free-volume hole model while it could be from the bulk in the hot model. The abstraction process, which allows an emission of epithermal Ps from the surface, is supported by the results of Ps energy spectra emitted from an epoxy surface [30]. In a reported Ps-TOF (time-of-flight) experiment [30], the Ps energy was found to be widely distributed from 100 eV to the thermal energy with an incident energy of 200 eV. The most populated energy of re-emitted Ps lies between a few eV and 100 eV. However there is no distinct energy peak which might correspond to the Ore gap (hot model) and also there is a very small distribution at the thermal energy (spur model). This observation is consistent with AMOC (age–Momentum–correlation) results in molecular systems [31] that Ps starts to thermalize at an energy level on the order of 10–30 eV.

It will be very interesting to perform parallel experiments on the same polymer with both Ps-TOF and AMOC in order to address the possibility of the Ore model involvement in Ps formation of polymers. However, the polymer surface is rather complicated compared with metal or semiconductor surfaces. Experimental detection of the Ore gap on polymer surfaces may be rather difficult. The suitability of the free-volume hole model in polymers has received great support from many experimental observations in the bulk. For example, the Ps formation is expected to be anti-correlated with the packing efficiency of molecular structure. An excellent anti-correlation exists in a series of polycarbonate-based polymers [32]. Also, the Ps formation is expected to be difficult for crystalline polymers where there is no free volume. Excellent anti-correlation between  $I_3$  and degree of crystallinity has been

observed in semi-crystalline polymers [33,34]. Thirdly, many existing temperature and pressure studies all show that  $I_3$  correlates nicely with the expected variations of fraction of free volumes and holes in similar series of polymers [1–10].

While this evidence provides a possibility that  $I_3$  could be a measure of the amount of free volume and holes in polymers based on the free-volume hole model for Ps formation, the development of a quantitative equation between  $I_3$  and the fraction of holes needs to consider many factors: (1) The trapping cross section of the positrons to form Ps depends on the size of holes. (2) The possibility of de-trapping Ps after it is formed, particularly in a very small hole (<0.2 nm). (3) The chemical quenching and inhibition of Ps need to be worked out for polymers consisting of strong Ps interaction groups and structures [13,25]. Only in polymers with a weak Ps interacting system (such as polyurethane, which consists of covalent bonds of O, H, N and C atoms) could the obtained o-Ps lifetime and intensity be interpreted in terms of the current free-volume hole model. In general, a semi-empirical equation of correlation between o-Ps parameters and hole properties could be worked out by including some other physical parameters, such as thermal expansivity and bulk compressibility.

#### 4. Conclusion

We present the results from positron annihilation study of polyurethane film using the PAL, DBES and slow positron beam methods. The variation of o-Ps intensity as a function of incident energy is consistent with the free-volume hole model for Ps formation in polymers. The result shows that the spur process does not play a significant part in Ps formation in polymers. The free-volume hole model provides a hope that PAL will provide a measure of the number of free volumes and holes in polymers. Further systematic studies of PAL and DBES in polymeric systems with well characterized functional groups will very helpful to develop PAS as a sensitive tool to characterize free volume and hole properties in polymeric materials. Applications of this technique to industry for coatings, membranes and gas separation are promising in the near future.

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